



**AL-IMAM MOHAMMAD
IBN SAUD ISLAMIC UNIVERSITY
COLLEGE OF SCIENCE
DEPARTMENT OF CHEMISTRY**

USE OF GREEN CHEMISTRY IN CORROSION INHIBITION OF IRON

A GRADUATION RESEARCH PROJECT

**SUBMITTED TO THE DEPARTMENT OF CHEMISTRY IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE COMPLETION OF
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DEDICATION

I DEDICATE THIS WORK TO DR MY SINCEREST APPRECIATION GOES TO HIM, FOR HIS PATIENCE, ADVICE, GUIDANCE, AND ATTENTION TO DETAIL THROUGHOUT MY RESEARCH. I AM ALSO DEEPLY GRATEFUL TO MY PARENTS, MY BROTHERS AND MY FRIENDS FOR THEIR INVALUABLE HELP AND THEIR PATIENCE.

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ABSTRACT

Abstract:

The corrosion behaviour of mild steel in 0.10 M hydrochloric acid (HCl) and 0.10 M nitric acid (HNO₃), in presence of inhibitors (sodium sulfite, hydrazine and Gum Arabic) has been studied. Specimens were exposed in the acidic media with and without inhibitors for one day and corrosion rates evaluated, using the weight loss method and corrosion current calculations. It was observed that nitric acid environment was most corrosive to both steels because of its oxidizing nature compared to hydrochloric acid. The rate of metal dissolution decreased with increasing concentration of the inhibitors in HCl. In HNO₃ the inhibitors showed less or no inhibition.

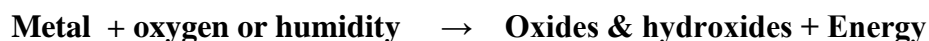
مستخلص البحث :

في هذا البحث تم دراسة تآكل الحديد في وسط حمضي . تمت إضافة مثبطات للتآكل في هذه الأوساط والمحاليل وتم تحديد كمية الحديد المتآكل في كلا من المحاليل النقية والمحاليل المحتوية على مثبطات التآكل . وتم حساب كل معاملات التآكل للحديد وتم حساب درجة منع التآكل لكل من المركبات .

CHAPTER ONE:

1.0 Introduction

Metals usually corrode to their oxides and hydroxides in an spontaneous natural phenomenon, in presence of oxygen, humidity and acidic gases at the environment around them. The corrosion is in fact an electrochemical reaction that can be presented as follows:.



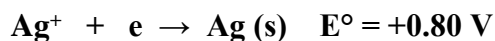
Looking at iron (Fe) as an active element (with negative reduction potential), it gets oxidized according to the reaction:



According to thermodynamic rules, the free energy change relation to potential (1.2), this reaction is nonspontaneous ($\Delta G^\circ > 0$). This implies that oxidized form of iron is more stable than the metallic form [Fe (s)].

$$\Delta G^\circ = - nFE^\circ \dots\dots\dots (1.2)$$

On the other hand noble metals such as silver are stable as metal as can be seen from its reduction potential;



where the positive value of E° indicates a negative value free energy. This fact shows that noble metals such as silver are stable as metals. On the other hand, less noble or active metals such as iron need protection against corrosion. One of the approaches is the use of inhibitors.

Chapter Two:

2.0 Literature review

2.1 Corrosion:

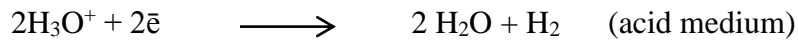
But noble metals, all metals commonly used in industries suffer from corrosion in their operation and environment. Bridges and pipelines and other metal structures are exposed to corrosive environments that reduce their duration life. This is clear from the large quantity of corrosion products that indicate the severity of the problem. Therefore, loss due to corrosion is an alarming engineering problem and the national economies therefore have to suffer great losses due to corrosion. Protection of metals and alloys from corrosion is therefore a subject of great technological and industrial importance and an enormous amount of research efforts have been directed towards the study of the process of corrosion and the stability of the materials in different environments.

Corrosion is a significant destructive phenomenon in science and industry [1,2]. In industries such as petrochemical industry, power generation, underground structures, chemical and oil industries, metals are used in over 90% of construction process [3]. Iron and steel are the most commonly used materials in the fabrication and manufacturing of oil field operating platforms because of their availability, low cost, ease of fabrication, and high strength. Most industrial media are usually rich in elemental gases, inorganic salts, and acidic solutions most of which influence corrosion rates, and mechanisms. Metals are usually exposed to the action of bases or acids in the industries. Processes in which acids play a very important role are acid pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling [4]. The exposures can be severe to the properties of the metals and thus lead to sudden failure of materials in service. There is therefore the need to study the corrosion behaviour of metals when exposed to various environments, as this is an

important factor in material selection that determines the service life of the material.

Mild steel and high carbon steels are classified as ferrous metals (they contain a large percentage of iron).

In practice the cathodic reactions that occur in aqueous solutions are reduction of either H_3O^+ or dissolved oxygen.



2.2 Thermodynamics of Corrosion

Generally, metallic corrosion in aqueous media is the resultant of two electrochemical reactions, namely metal dissolution and hydrogen evolution i.e.,



According to thermodynamics, for the above process to be spontaneous

$$\Delta G = -nF\Delta E \quad (2.2)$$

2.3 Kinetics of Corrosion

In corrosion process the rate is expressed in terms of current.

2.4 Types of corrosion [4]

The main types of corrosion are: uniform corrosion, galvanic corrosion, pitting corrosion, parting corrosion, stress corrosion cracking, erosion corrosion.

Table 2.1: Types of corrosion

Type of Corrosion	Material System	Driving Force	Control Point	Remark
Uniform/General Corrosion	All Metals in Atmospheric Environment	- Atmospheric - Temperature	- Painting - Hot Dip Galvanizing	- Corrosion Cost of this form about 50% of the total corrosion cost - Seldom lead to failure
Intergranular Corrosion	Al Alloys, Ni-Cr Austenitic Stainless Steel Acids Containing Oxidizing Agents (sulfuric, phosphoric), Hot Organic Acid. High Cl Content Seawater	- Third Phase Precipitate - Temperature	- Heat Treatment in Manufacturing - Welding during Fabrication	- Loss of Strength and Ductility - Severe attack can lead to failure
Galvanic Corrosion	Galvanic Coupling Materials e.g. Fe with Cu, Carbon steel with Stainless Steel	Different Metal in electrolytic solution	- Proper Design; - Rivetting/Joining Materials; - Insulating Coupling Materials	Moderate effect but can be detrimental for a longer period
Crevice Corrosion	Metal to Metal/Non Metal in Electrolyte Metal in two Electrolyte Aluminium and Stainless Steel in Seawater	- Small Gap in electrolyte (<3,18mm) - Stagnant Fluid	- Proper Design - Gasketing Materials - Proper Drainage Practice	Moderate effect but can be detrimental for a longer period
Pitting	Stainless Steel and Aluminium in chloride or bromide environment (water/soils)	- Surface Irregularities - Presence of Cl or Br Ion - Chemical Composition - Temperature	- Surface Quality Control - Proper Welding Practice - Proper Material Handling - PREN (Material Selection) - CPT (Critical Pitting Temperature)	Severe attack can lead to failure (second biggest corrosion failure)
Erosion Corrosion Tribo-Corrosion	Carbon Steel, Stainless Steel in flowing fluid containing abrasives	Synergy effect of passive film breakdown by abrasive and localized corrosion	Corrodent; turbulency Corrodent impingement in elbow and tees	Severe attack can lead to failure
Stress Corrosion Cracking (SCC)/ HE-SCC	Stainless Steel, Carbon Steel in High pH (pH >9,3) - 600 - 750 mV - Temperature Sensitive Near Neutral pH (5,5 - 7,5) - Free Potential - Non-Temperature Sensitive	- Microstructure - Temperature Region - Existence of Residual Stress - Suitable pH - Presence of H ₂ S, Chloride ion - Residual Stress	- Microstructure Control during - H ₂ S Content & Temperature - Operation Temperature	- Biggest Cause of Corrosion Failure - SCC found in gas and liquid pipelines - In Canada since 1977: recorded 22 catastrophic failure (12 rupture, 10 leaks)
Biological Corrosion/ Microbial Induced Corrosion	All Metals in Environment with: - Sulfate Reducing Bacteria - Sulphur/Sulfate Oxidizing Bacteria - Fe/Mn Oxidizing Bacteria - Organic Acid Producing Bacteria	- Gravitational & Pellicular Water - pH 6 - 8 - Potential -42mV to 820mV - Temperature: 20 °C - 45 °C	Application of Organic Coating Cleaning Practice Use of Biocide	In US, \$1.2 billion SPENT annually on biocidal chemicals to fight MIC.

2.5 Factors affecting corrosion

There are a number of mutually interdependent factors relating to metal as well as the medium that greatly affect the corrosion process. They are classified as primary factors (relating to metal) and secondary factors (relating to the medium).

2.5.1 Primary Factors

a) Nature of the Metal

Electrode potential can tell whether a certain metal has the tendency to corrode in an aqueous solution or not. Each element has a characteristic electrode potential as

listed out in the “Electrochemical series”. Accordingly, metals with more positive potentials are relatively stable e.g. noble metals, and those with more negative potentials are unstable e.g. zinc and iron.

b) Surface State of the Metal

The surface condition of the metal can greatly influence its tendency to corrode or not. Smooth and polished surfaces resist corrosion in contrary to a rough surface containing various types of imperfections such as cleavage steps, dislocations, point defects etc. is prone to severe attack.

c) Protective films

Certain metals like Cr have a tendency to form oxide protective films on the surface that act as physical barriers between the metal and the medium thereby curtailing corrosion.

2.5.2 Secondary Factors

a) Dissolved oxygen

Dissolved oxygen in the medium plays an important role when corrosion involves its reduction as the cathodic reaction

b) pH

For metals like iron, magnesium, etc., hydrogen evolution is the thermodynamically favoured cathodic reaction. Corrosion of these metals in acidic medium is therefore highly pH dependent. A decrease in pH (acidic condition) facilitates the rate of hydrogen evolution and hence increases the corrosion rate of metals. At the other side a high basic medium accelerates the reduction of oxygen and consequently increases the metal corrosion behavior.

c) Temperature of the medium

An increase in the temperature of the medium usually enhances the rate of corrosion process. This is especially significant in media in which corrosion is accompanied by hydrogen evolution.

d) Effect of other ions present in solution

The presence of other ions usually Fe^{+3} , NO_3^- , Cl^- , SO_4^{-2} etc, in certain concentration ranges affect the rate of corrosion. For instance Cl^- ions interfere with the formation of protective films on metals such as iron, aluminium and copper and cause extensive damage because of the specific activity of Cl^- . Similar effects with less severity are observed in the presence of SO_4^{-2}

2.6 Corrosion control

Corrosion control is achieved by several methods depending upon the type of corrosion and environmental conditions. Some methods commonly used to control corrosion are:

- i. Cathodic protection
- ii. Anodic protection (Passivation)
- iii. Coatings (metallic, Organic, Inorganic, ...etc)
- iv. Chemical control of the environment using inhibitors.

Of these the last method has been extensively investigated.

2.7 Types of Inhibitors

The practice of using of inhibitors is common for corrosion prevention or reduction. An inhibitor is defined as “*a chemical substance, organic or inorganic in nature added in traces to the corrosive medium in order to retard the corrosion rate*”. Corrosion inhibition utilizing inhibitors can therefore be defined as the treatment of a metal surface by the addition of low percentages of chemicals to the environment to control

the corrosion process. Based on the mode of action, corrosion inhibitors are classified as

- (i) Anodic inhibitors
- (ii) Cathodic inhibitors and
- (iii) Mixed (adsorption) inhibitors.

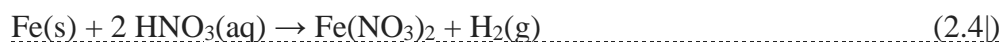
2.8 Iron corrosion in acids

Iron displaces hydrogen from hydrochloric acid to form pale green iron (II) chloride:



The chloride crystallizes as $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$. Exposure to air gradually oxidizes the iron (II) to FeCl_3 and Fe_2O_3 . Oxidizing FeCl_2 with Cl_2 produces orange-yellow FeCl_3 , which has metal-nonmetal bonds with covalent character.

Similarly iron corrodes in nitric acid



The above anodic reactions are accompanied with cathodic reactions such as the oxygen reduction



Or H reduction to evolve hydrogen



2.9 Corrosion rate measurement:

There are two main methods for the measurement of corrosion rate.

1. Weight loss methods:

Here the corrosion rate is measured by the amount of metal (mg) dissolved in a specific period of time. It can also be calculated as mm/year:

$$mm / year = \frac{87.6xW}{dxAct} \quad (2.7)$$

where:

W = weight loss (mg).

d = metal density (g.cm⁻³).

A = metal sample surface area (cm²).

t = immersion time (h).

2. Electrochemical methods:

In these methods the rate is expressed as corrosion current (i_{corr}). The i_{corr} can be obtained from the weight loss by the formula:

$$i_{corr} = \frac{nxFxW}{mXt} \quad (2.8)$$

where:

n = number of electrons.

F = Faraday's constant.

W = weight loss (g).

m = atomic mass of the metal.

t = time of immersion (s).

The addition of inhibitors reduces the rate of corrosion and consequently the inhibition efficiency is calculated as:

$$Inhibition \% = \frac{W_0 - W}{W_0} \quad (2.9)$$

where:

W_0 = corrosion rate (mg/h) **without** inhibitor.

W = corrosion rate (mg/h) **with** inhibitor.

Also it can be calculated from the corrosion current values:

$$Inhibition \% = \frac{i_0 - i}{i_0} \quad (2.10)$$

where:

i_0 = corrosion rate (mg/h) **without** inhibitor.

i = corrosion rate (mg/h) **with** inhibitor.

Mild steel is an important industrial metal used in various applications. Hydrochloric acid solutions are widely used for the pickling, cleaning, descaling and etching of mild steel [5]. Various methods are followed to stop metals corrosion but the use of inhibitors is the most practical methods for preventing their corrosion, especially in acidic media [6]. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms [7] Compounds containing heteoatoms like sulfur and nitrogen are considered to be very effective corrosion inhibitors [8].

The inhibitive reactivity of an inhibitor is fundamentally affected by the molecular structure of the inhibiting molecules. Most prominent corrosion inhibitors are organic compounds containing nitrogen, sulphur, oxygen, and phosphorus in their functional groups [9]. The mechanism of these compounds has been proposed to be the adsorption, by means of lone pairs of electron, of the organic functional groups on the metal surfaces [10].

Adsorption: [4]

Inhibitors retard corrosion by adsorption of the surface of metals to isolate it from the corrosion medium. Two types of corrosion modes are there,

physisorption and chemisorption. The table below compares these two types.

Table (2.1): Chemisorption and Physisorption

Physisorption	Chemisorption
Low heat of adsorption usually in range of 20-40 kJ/mol	High heat of adsorption in the range of 50-400 kJ/mol
Force of attraction are Vander Waal's forces.	Forces of attraction are chemical bond forces.
It is reversible	It is irreversible
It is usually takes place at low temperature and decreases with increasing temperature.	It takes place at high temperature.
It forms multimolecular layers.	It forms monomolecular layers.
It does not require any activation energy.	It requires high activation energy.
It is not very specific.	It is highly specific.

The most frequently used adsorption isotherms are Langmuir, Temkin, Frumkin and Freundlich isotherms.

The research objective:

1. To study the corrosion of mild steel in hydrochloric and nitric acids.
2. To investigate the effect of the inhibitors i.e. sodium sulfite, hydrazine and gum Arabic on the corrosion of mild steel in the acidic media.
3. To determine the amount of iron dissolved with and without inhibitors using spectrophotometric methods..
4. To calculate the corrosion rate and inhibition efficiency of these inhibitors.
5. To study the inhibitors adsorption onto the surface of the metal.

Chapter Three:

3.0 Experimental:

3.1 Chemical:

The chemicals HCl, HNO₃, sodium sulfite, hydrazine were from analar grade. The gum was purchased from a retail shop. Distilled water was used to make all solutions except sea water.

3.2 Corrosion studies:

To study the corrosion and corrosion inhibition, about 2.0 cmx2.0 cmx0.20 cm sheet of mild steel was cut. The sheet was immersed in 25.0 ml solution of pure HCl and HNO₃ without and with different concentration of inhibitor for one day. The solution were then collected and kept in a plastic container for further analysis.

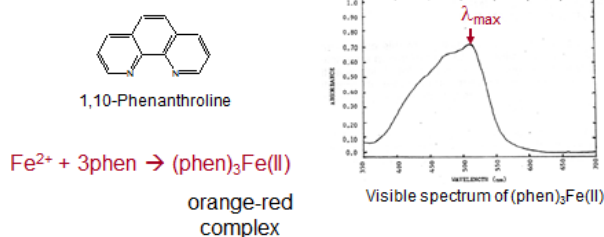
3.3 Iron determination: [11]

Iron (II) reacts with 1,10-phenanthroline to give an orange-red complex that absorbs at 515 nm. The complex is stable at pH 2 - 9 for long time. Due to the tendency of Fe⁺² to get spontaneously oxidized to Fe⁺³ as the electrochemical reaction has positive value:



To avoid this reaction Fe^{+3} is reduced using hydroxylamine hydrochloride.

Tris(1,10-phenanthroline)iron(II)



4



Fig 3.1: Iron , 1,10 phenanthroline complex

Apparatus

1. A spectrophotometer (in the visible range).
2. Sample glass cuvettes.
3. Volumetric flaks.
4. Beakers.
3. pH Meter.

Chemicals and Reagents

1. Acetate buffer pH 4.0. (65 ml of 0.10 M acetic acid and 35 ml sodium acetate).
2. 0.5 M Hydroxylamine hydrochloride.
3. $\text{Fe}(\text{NH}_4)_2 (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ standard solution (100 ppm).

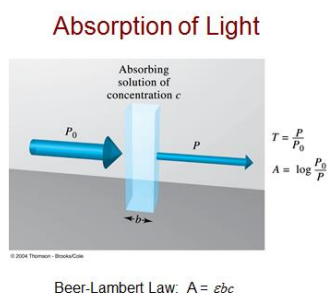
4. 5×10^{-4} M 1,10- phenanthroline solution.

Buffer solution preparation:

Procedure

1. About 5 mL of Fe^{2+} standard solution was added to 5 mL of the acetate solution into a 25 mL volumetric flask.
2. Exactly 2 mL of hydroxylamine hydrochloride solution was added followed by a 5 mL portion of the standard 1,10-phenanthrolyine solution.
3. The volume was adjusted to the mark using distilled water and allow to stand for 10 min.
4. The blank was placed in one of the absorption cells provided and adjust the absorbance reading to zero at 515 nm.
5. The previous steps were followed to determine the
7. The results were plotted on an x-y graph with absorbance on the y axis and wavelength on the x axis and draw the absorption spectrum.

The concentration of Fe^{+2} in the samples was calculated using Beer's law:



$$A = \epsilon bC \quad (3.2)$$

where:

A = absorbance.

ϵ = absorbtivity coefficient or molar absorption coefficient

($M^{-1}.cm^{-1}$).

b = path length or cell length (cm).

C = analyte concentration (M).

Chapter Four:

4.0 Results and Discussion:

The absorbance versus concentration of the standards is given in the table below:

Table (4.1): Concentration vs Absorbance of Fe (II) standards

Conc. (ppm)	Abs.
0	0
2	0.47
4	0.94
6	1.36
8	1.83
10	2.14

The standard calibration curve of the iron absorption is shown in figure (4.2).

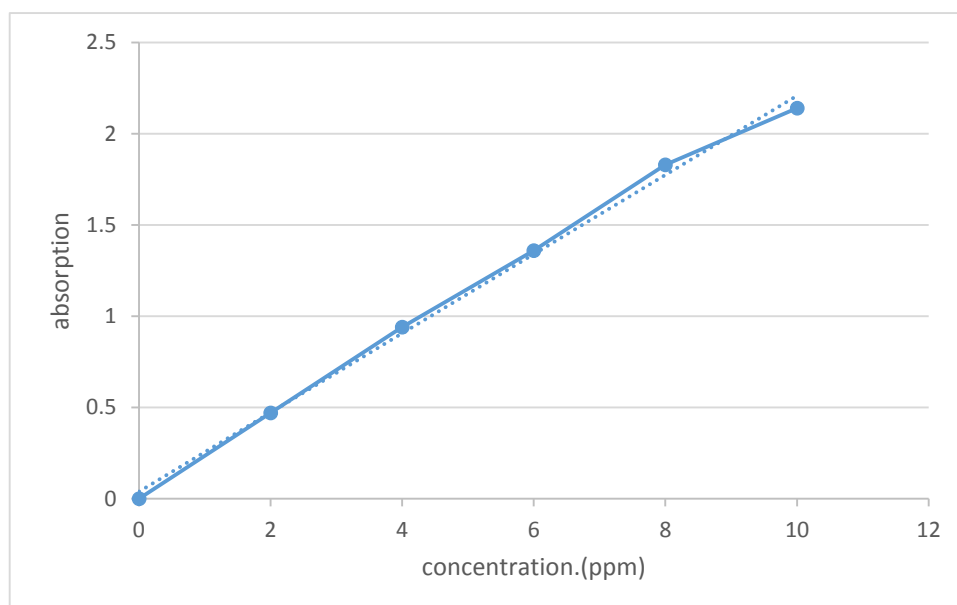


Fig. (4.2): Standard calibration curve for iron absorption

The curve was used to obtain the concentration of iron in the samples. The amount of iron dissolved was calculated using the formula:

$$\text{Amount of Fe (mg)} = C \times V \times D_f \quad (4.1)$$

where:

c = concentration (mg.L^{-1})

V = volume of sample (L)

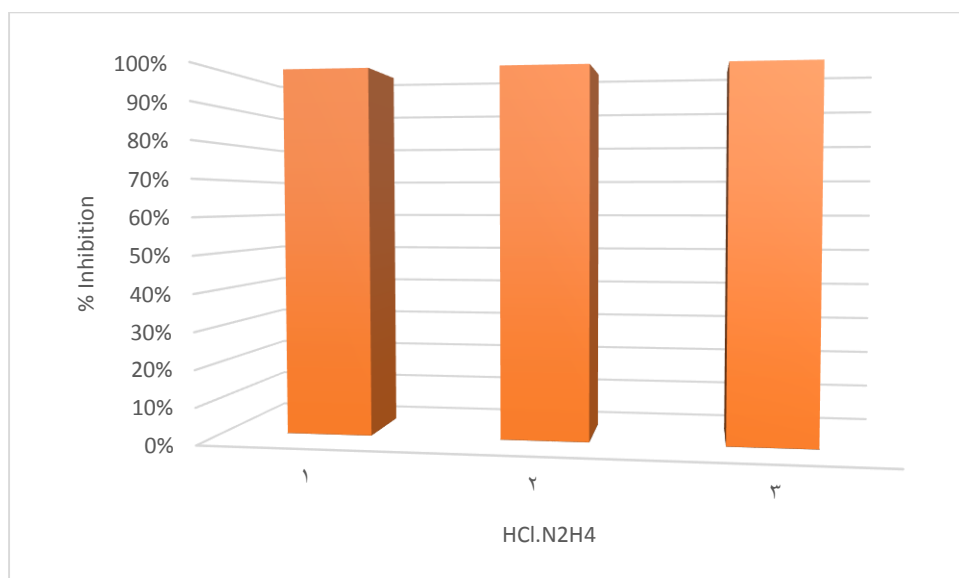
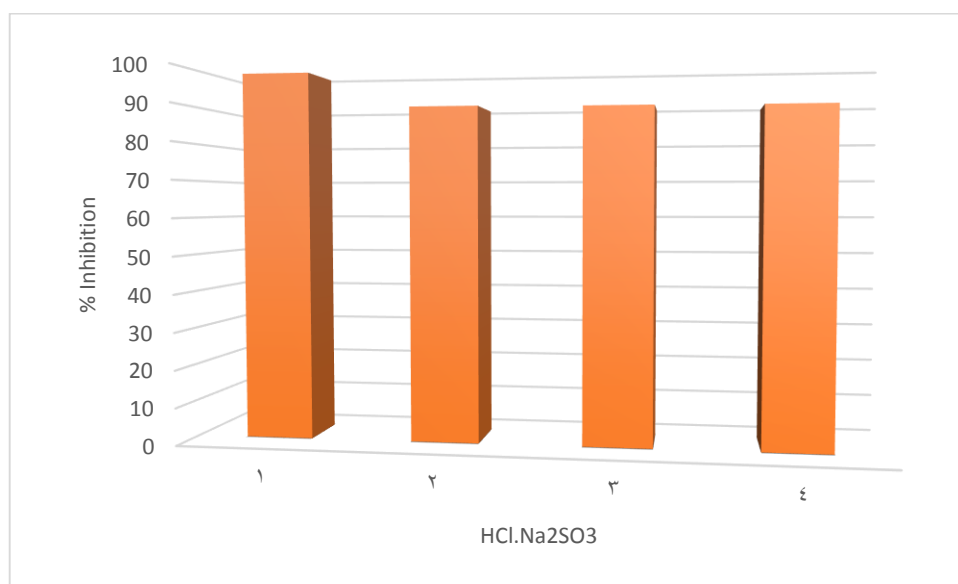
D_f = dilution factor

Table (4.2) depicts the amount of iron corroding in pure 0.10 M HCl and 0.10 M HNO₃ without and with inhibitors. The amount of iron corroded has obviously decreased with the addition of hydrazine, sodium sulfite and gum Arabic relative to the HCl alone. The amount of iron dissolved at different concentrations of sodium sulfite was found to increase as the concentration was reduced. Similarly the corrosion inhibition efficiency reduces with the sodium sulfite solution dilution. The inhibition efficiency of iron in hydrazine solutions was high even at lower concentration. The table also shows the inhibition efficiency of Gum Arabic at different mass ratio. This may be due to the formation of a protective film on the surface of the iron sheets.

Table (4.3): Weight loss and percentage corrosion inhibition of iron in the different solutions

Solution	Fe (mg/h)	% Inhibition
HCl pure	0.1380	
1 M Na ₂ SO ₃	0.0023	98.70
0.5 M Na ₂ SO ₃	0.0147	89.35
0.25 M Na ₂ SO ₃	0.0151	89.05
0.125 M Na ₂ SO ₃	0.0153	88.90
1 M N ₂ H ₄	0.0002	99.85
0.5 M N ₂ H ₄	0.0063	95.43
0.25 M N ₂ H ₄	0.0082	94.05
0.50 g Gum Arabic	0.0146	89.42
0.25 g Gum Arabic	0.0148	89.20
0.13 g Gum Arabic	0.0152	88.00
HNO ₃ pure	0.170	
1 M Na ₂ SO ₃	0.0095	94.41
0.5 M Na ₂ SO ₃	0.0135	92.05
0.25 M Na ₂ SO ₃	0.0142	91.60

0.125 M Na ₂ SO ₃	0.0171.	90.00
1 M N ₂ H ₄	0.0192	88.9
0.5 M N ₂ H ₄	0.101	40.59
0.25 M N ₂ H ₄	..	000
0.125 M N ₂ H ₄	...	000
0.50 g Gum Arabic	0.0133	92.17
0.25 g Gum Arabic	0.0171	88.90
0.13 g Gum Arabic	0.179
0.06 g Gum Arabic



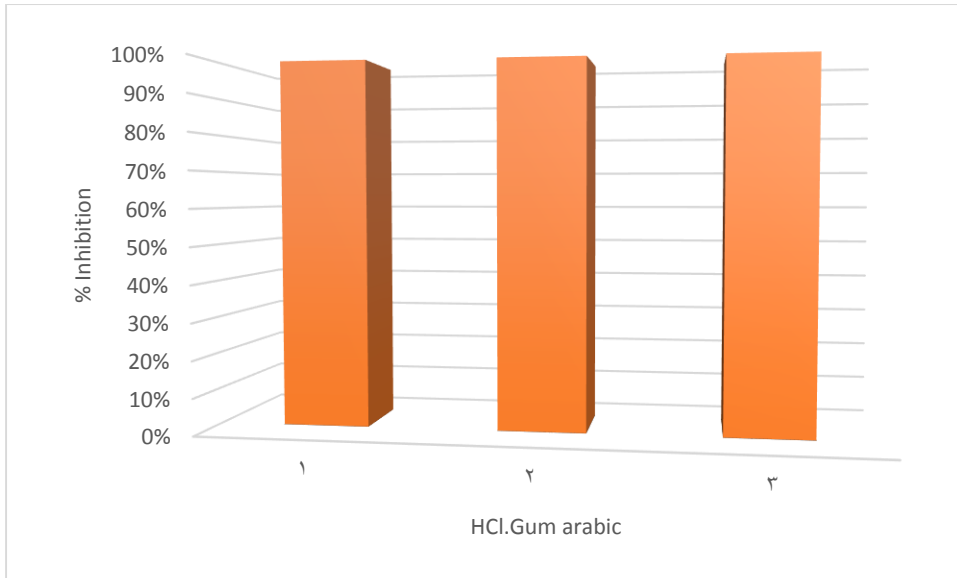
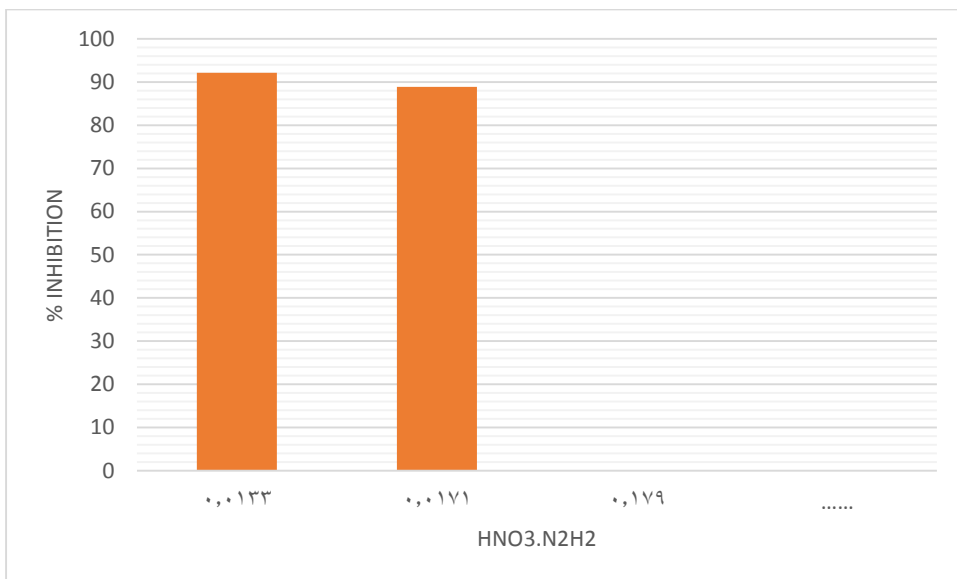
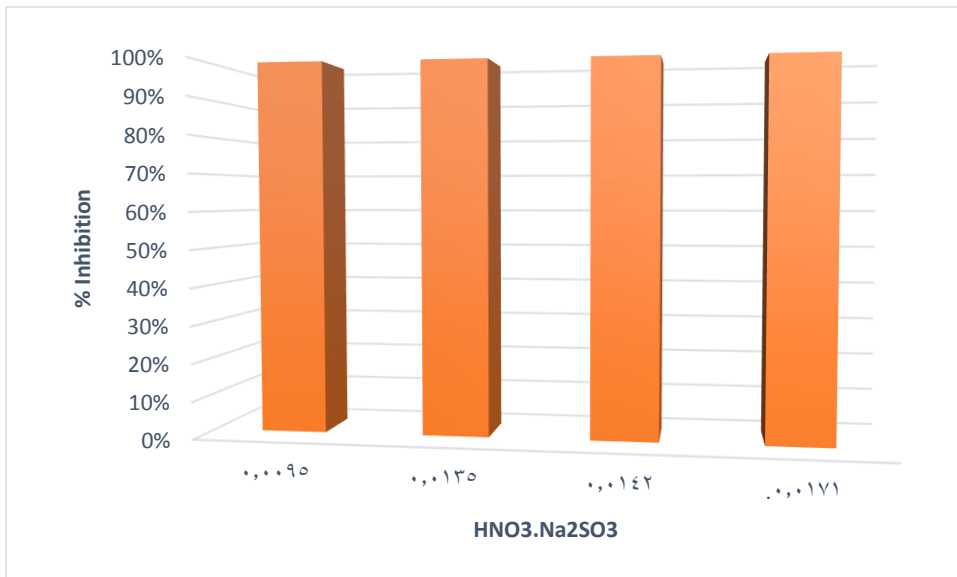


Fig. (4.3): Corrosion Inhibition of inhibitors in 0.10 M HCl



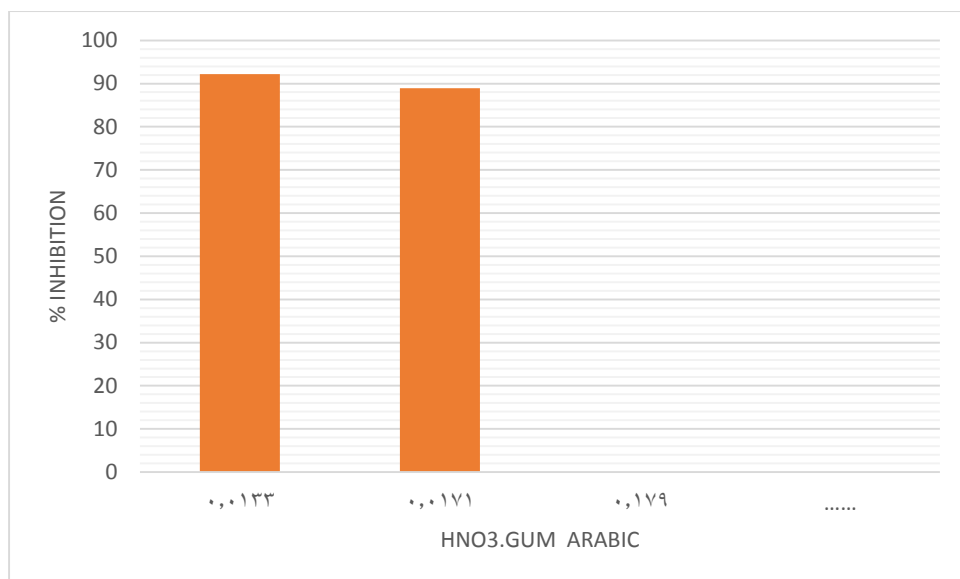


Fig. (4.3): Corrosion Inhibition of inhibitors in 0.10 M HNO₃

The weight loss and the percentage inhibition of the same compounds under study in 0.10 M HNO₃ is also shown in the table. The amount of iron dissolved was found to increase in nitric acid as it is strong oxidizing agent. The amount of iron dissolved at different concentrations of inhibitors was found to increase as the concentration was decreased. Similarly the corrosion inhibition efficiency reduces with the inhibitors dilution. The hydrazine and sodium sulfite also shows less weight loss and high inhibition concentration, indicating their ability to protect steel in basic medium is high.

Table (4.4): Corrosion rate in (mm/year) for iron in different solutions

Solution	Fe (mg/h)	Corrosion Rate (mm\Year)
HCl pure	0.1380	0.014
1 M Na ₂ SO ₃	0.0023	0.00023
0.5 M Na ₂ SO ₃	0.0147	0.00490
0.25 M Na ₂ SO ₃	0.0151	0.00153
0.125 M Na ₂ SO ₃	0.0153	0.00155
1 M N ₂ H ₄	0.0002	0.00002
0.5 M N ₂ H ₄	0.0063	0.00063
0.25 M N ₂ H ₄	0.0082	0.00083
0.50 g Gum Arabic	0.0146	0.00148
0.25 g Gum Arabic	0.0148	0.00150
0.13 g Gum Arabic	0.0152	0.00541
HNO ₃ pure	0.170	0.0172

1 M Na ₂ SO ₃	0.0095	0.00096
0.5 M Na ₂ SO ₃	0.0135	0.00137
0.25 M Na ₂ SO ₃	0.0142	0.001440
0.125 M Na ₂ SO ₃	0.0171	0.00173
1 M N ₂ H ₄	0.0192	0.00195
0.5 M N ₂ H ₄	0.101	0.0102
0.25 M N ₂ H ₄	0	0
0.125 M N ₂ H ₄	0	0
0.50 g Gum Arabic	0.0133	0.00135
0.25 g Gum Arabic	0.0171	0.00173
0.13 g Gum Arabic	0.179	0.0182
0.06 g Gum Arabic	0	

In table (3), the corrosion current, corrosion current density and percentage inhibition of iron corrosion in pure corroding solutions and solutions containing inhibitors are shown. The values were obtained using equations 2.7, 2.8 and 2.9. Corrosion current results from the process of corrosion and therefore increases with the extent of corrosion was calculated using equation 2.10. From the table we can see that the corrosion current and current density are highest when iron is immersed in pure HCl and HNO₃. This is an indication of the high corrosiveness of these acidic solutions. The addition of inhibitors had greatly reduced the corrosion current and current density. This is an indication of the inhibition action of these compounds. The percentage inhibition calculated using the corrosion current values were almost equal to those obtained from the weight loss measurements.

Table (4.5): Corrosion current and current density for iron in different solutions

Solution	i_{corr} (mA)	% Inhibition	j (mA/cm ²)
HCl pure	5.506		1.377
1 M Na ₂ SO ₃	0.009	98.70	0.002
0.5 M Na ₂ SO ₃	0.586	89.35	0.147
0.25 M Na ₂ SO ₃	0.602	89.05	0.151
0.125 M Na ₂ SO ₃	0.610	88.90	0.153
1 M N ₂ H ₄	0.008	99.85	0.002

0.5 M N ₂ H ₄	0.025	95.43	0.006
0.25 M N ₂ H ₄	0.033	94.05	0.008
0.50 g Gum Arabic	0.583	89.42	0.143
0.25 g Gum Arabic	0.591	89.20	0.148
0.13 g Gum Arabic	0.606	88.00	0.152
HNO ₃ pure	6.78		1.700
1 M Na ₂ SO ₃	0.379	94.41	0.095
0.5 M Na ₂ SO ₃	0.539	92.05	0.135
0.25 M Na ₂ SO ₃	0.567	91.60	0.142
0.125 M Na ₂ SO ₃	0.682	90.00	0.171
1 M N ₂ H ₄	4.030	88.9	0.168
0.5 M N ₂ H ₄	4.030	40.59	1.008
0.25 M N ₂ H ₄
0.125 M N ₂ H ₄
0.50 g Gum Arabic	0.531	92.17	0.158
0.25 g Gum Arabic	0.682	88.90	0.171
0.13 g Gum Arabic
0.06 g Gum Arabic

From the data obtained for the corrosion of iron using the sodium sulfite, hydrazine and gum we can observe that they reduce the rate of iron corrosion in 0.10 M HCl and 0.10 M HNO₃. This may be explained by the adsorption of these compounds on the surface of iron. The lone pair of electron in the structure of these compounds can make them attracted to the metal surface by electrostatic forces [3, 6]. Therefore these compounds can make protective films that isolate the metal surface from the corrosion medium.

The less inhibition efficiency shown by gum solutions at lower concentration may have been due to the removal of the protective layer formed by the oxidizing nitric acid.

Adsorption Isotherms:

The most frequently used adsorption isotherms are Langmuir, Temkin, Frumkin and Freundlich isotherms. In order to obtain the adsorption isotherm, the degrees of surface coverage (θ) were calculated for various concentrations of the inhibitor from the weight loss data. Langmuir adsorption isotherm was tested to fit with the experimental data.

Langmuir adsorption isotherm is represented by following equation [12]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (4.2)$$

where K_{ads} is the adsorption equilibrium constant, θ is the degree of surface coverage and C is molar concentration of inhibitor used in the corrosive solution. A straight line was obtained by plotting C vs C / θ for the inhibitor used in study (Figure 4.4). This suggests that, the Langmuir adsorption isotherm provides the best description of the adsorption behavior. The degree of surface coverage (θ) for different inhibitor concentrations of cefadroxil was evaluated from weight loss data and listed in the Table 2. The slope of the isotherm graph reported in Table 4.5 is less than unity and this suggests the multilayer adsorption of the inhibitor molecule.

Table (4.6): C and C / θ for Na_2SO_3 adsorption on iron surface

C	1	0.5	0.25	0.13
C / θ	0.987	0.56	0.28	0.15

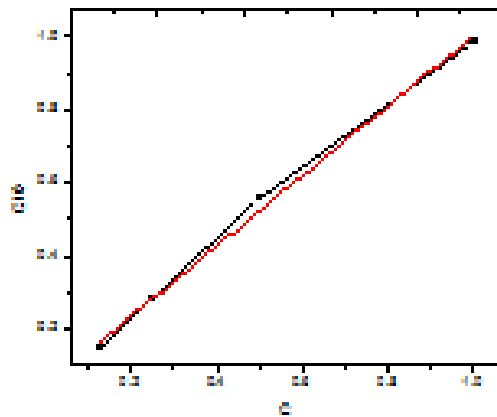


Fig. (4.6): Langmuir adsorption isotherm for Na_2SO_3 adsorption on iron surface

Table (4.7): Adsorption parameters for Na_2SO_3 adsorption on iron surface

Intercept	Slope	R^2
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0.043174	0.9585	0.993
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From equation 3.4:

$$\text{Intercept} = 1/K_{\text{ads}}$$

$$K_{\text{ads}} = 1/0.043174$$

$$K_{\text{ads}} = 23.16$$

The value of R^2 supports that the adsorption follows the Langmuir isotherm model.

From the value of the adsorption constant (K_{ads}), the free energy of adsorption can be calculated:

$$\Delta G = -RT \ln K_{\text{eq}}$$

$$\Delta G = - 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 303 \text{ K} \times \ln 23.16 = - 7916.21 \text{ J mol}^{-1}$$

The negative value of ΔG indicates spontaneous adsorption. The small value of ΔG is the sign of a physisorption process.

5.0 Conclusions:

1. The corrosion of iron (mild steel) in 0.1 M HCl and 0.10 M HNO₃.
2. The amount of iron dissolved was determined by spectrophotometric methods using 1,10-phenanthroline that complexes with Fe⁺² ions.
3. The inhibitors: sodium sulfite, hydrazine and gum Arabic were added to retard the corrosion process.
4. The weight loss, corrosion rate, inhibition efficiency, corrosion current and corrosion density were obtained.
5. The results showed that the compounds used could reduce the corrosion of iron in the different solution.
6. The adsorption was found to follow the Langmuir adsorption model. The adsorption constant and the free energy were obtained. The free energy value indicated the spontaneous nature of adsorption. The adsorption is physisorption.

6.0 Recommendations:

1. Study the corrosion of other metals in these solutions.

2. Use more techniques such as electrochemical polarization. Also the use of imaging techniques to study the structures of metals surfaces.

7.0 Acknowledgement:

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